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TECHNICAL REPORT #1

AN ORGANIC THIN FILM LASER DIODE: A NOVEL LIGHT SOURCE

by

N. Peyghambarian, N.R. Armstrong, H. Hall, A. Padias, S. Mazumdar

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Introduction

Our proposal to ONR focused on the development of an entirely new diode laser, based upon electroluminescent organic thin films. We proposed to develop new polymers for this important application. As shown below, we have made significant progress during the ten first months of this project toward the realization of these challenging objectives. We have successfully fabricated so far a promising LED based on a new aluminumquinolate derivative that emits in the blue-green and that can be dissolved in a polymer matrix and spin-cast.

It is clear that a diode laser based upon organic thin film electroluminescent materials will have to satisfy several different criteria: a) high electroluminescence efficiencies will have to be obtained, as with the best organic LED technologies known today, b) the device will have to allow for waveguiding of the emitted light within the luminescent layer with low absorption losses and high gain, and c) the stability of these structures will have to be at least as good as those of the best organic LED's, because of the electrical and optical perturbations that these materials will have to endure.

Our approach has been to produce new materials which will possess both the electrical and optical properties required for an organic laser diode, and to approach the fabrication of prototype devices based on these materials by two different technologies: by spin-coating and by vacuum evaporation. At the same time, we have been setting up a state-of-the-art technology based on a complete sample-preparation unit under controlled atmosphere. This technology is required to develop devices with a high stability and to test them rigorously. In addition, a systematic characterization of the energy levels of several electroluminescent materials has been undertaken with our UV-photoelectron spectroscopic facilities in order to screen existing and new materials. Finally, preliminary LED's have been fabricated by using different techniques and their electroluminescent properties have been characterized.

This progress report is divided into four sections which detail our efforts over the last ten months:

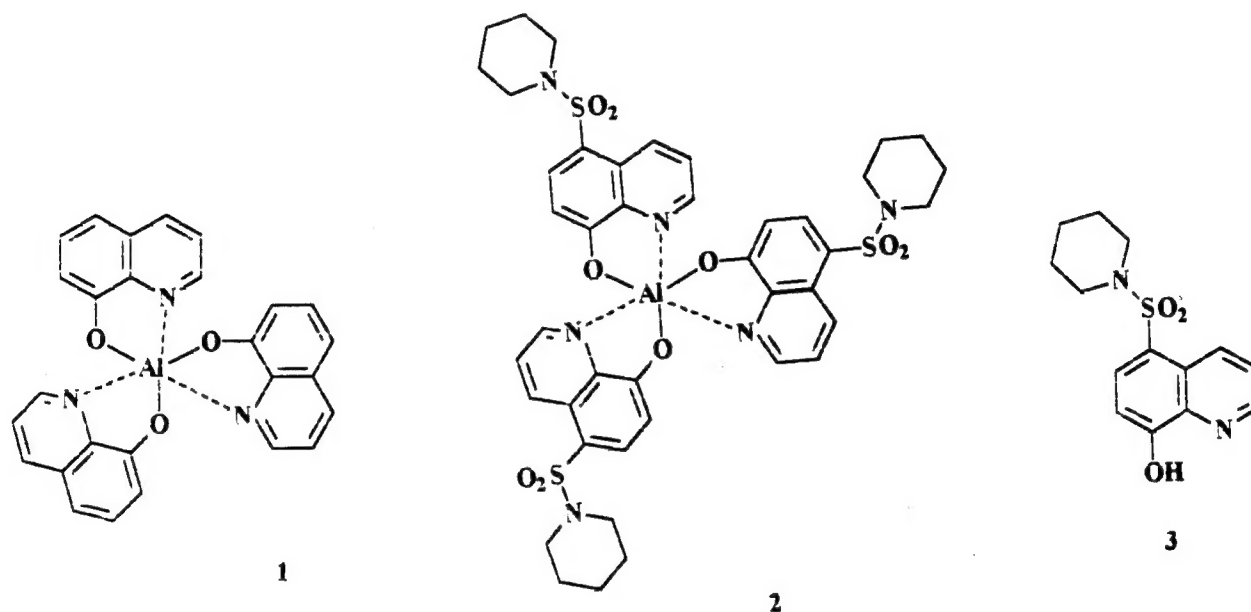
- A) Synthesis of new electroluminescent agents based upon aluminum quinolates.
- B) Development of the state-of-the-art technology required to produce prototype devices under controlled atmosphere.
- C) Characterization of the "band edges" for various electroluminescent materials and charge transport agents.
- D) Fabrication and characterization of blue-green emitting LED's: preliminary results.

A) Development of new electroluminescent materials based upon aluminum quinolates

To achieve our objective of incorporating the luminescent agent in a waveguiding polymer we realized that it would be necessary to either incorporate the agents directly into the polymer backbone (and retain good optical properties) or make polymer-soluble forms of luminescent agents which could be doped at high concentration into optical quality polymer matrices. We have adopted the second approach in the first phase of this project.

Metalloquinolates are known as materials with large luminescence efficiencies. Although there are a number of metalloquinolate derivatives suitable as electroluminescent materials in LED devices, all of the known derivatives emit light in the yellow to green region of the visible spectrum. There are none yet reported that reliably emit in the blue region.

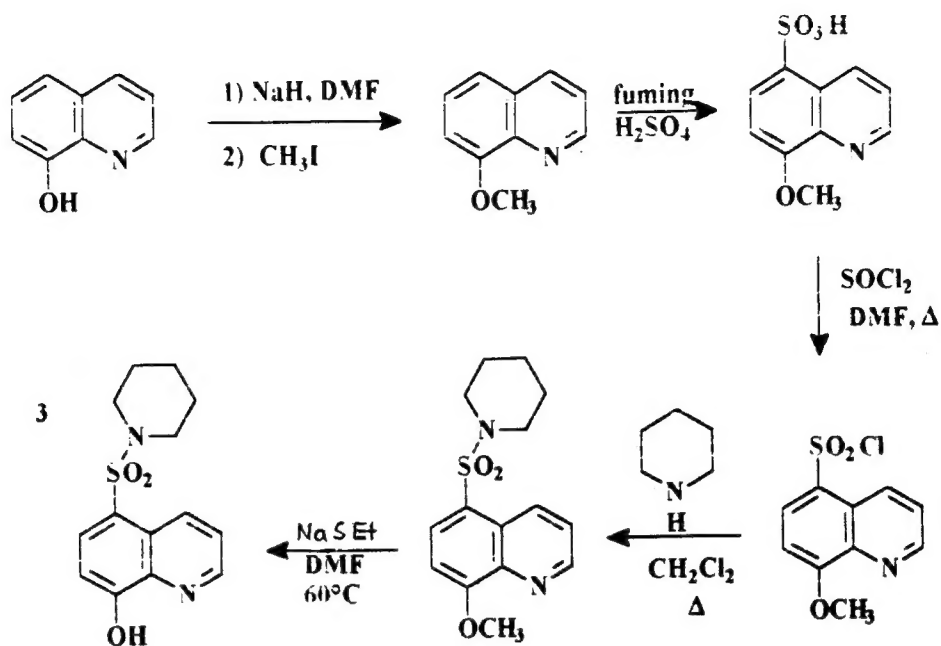
To influence the optical spectrum of the unsubstituted aluminum quinolate **1** (Alq_3), it is best to place electron-withdrawing or -donating groups in the 5-position of the quinoline ring. This maximizes the interaction of the substituent with the HOMO, thereby increasing or decreasing the HOMO-LUMO gap and thus blue- or red-shifting both the absorbance and emission spectra. At the same time, the solubility may be enhanced with a large aliphatic group on the substituent.



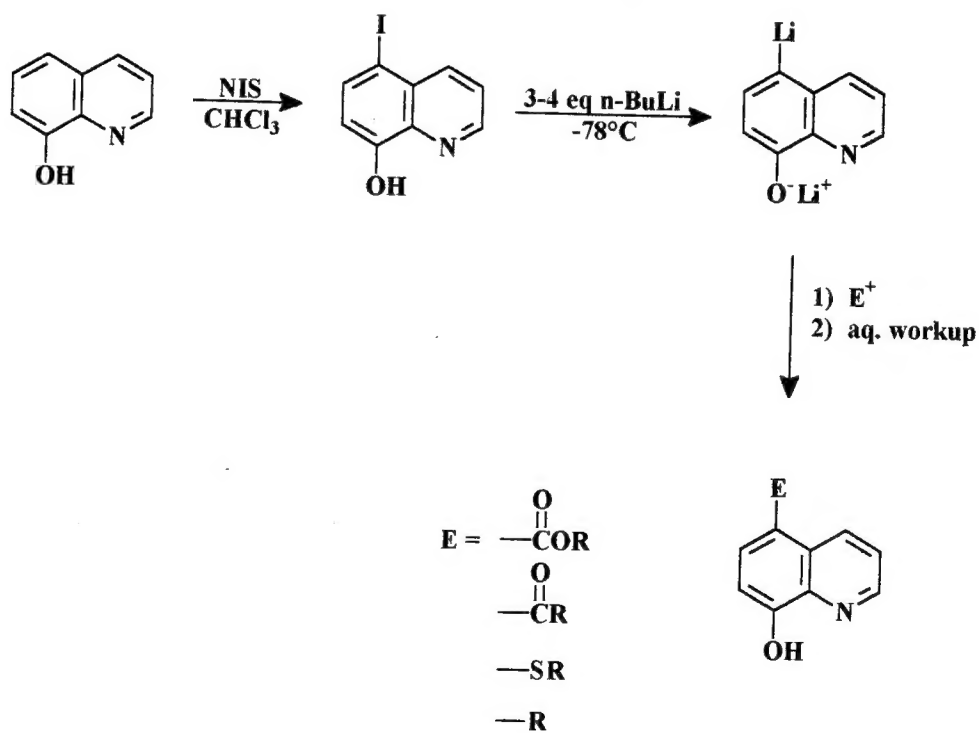
Recently, we have successfully synthesized aluminum quinolate **2** (Al(qS)_3) by the reaction of 8-hydroxyquinoline sulfonamide **3** with triethylaluminum in THF. **3** was prepared according to Scheme I.

Figure 1 compares the absorption and photoluminescence spectra of a thin film of crystalline Alq_3 and a thin film of Al(qS)_3 incorporated at ca. 50% (w/w) in poly(vinylcarbazole) (PVK). It can be seen that both the absorbance and the fluorescence of Al(qS)_3 are blue-shifted by 10 nm and 29 nm, respectively, compared with Alq_3 . Furthermore, the solubility of Al(qS)_3 in various solvents and polymers is also considerably enhanced over the unmodified Alq_3 , as a result of the aliphatic substituent.

Scheme I. Synthesis of Sulfonamide 3



Scheme II. Synthesis of 5-Substituted Quinolines via Lithiation



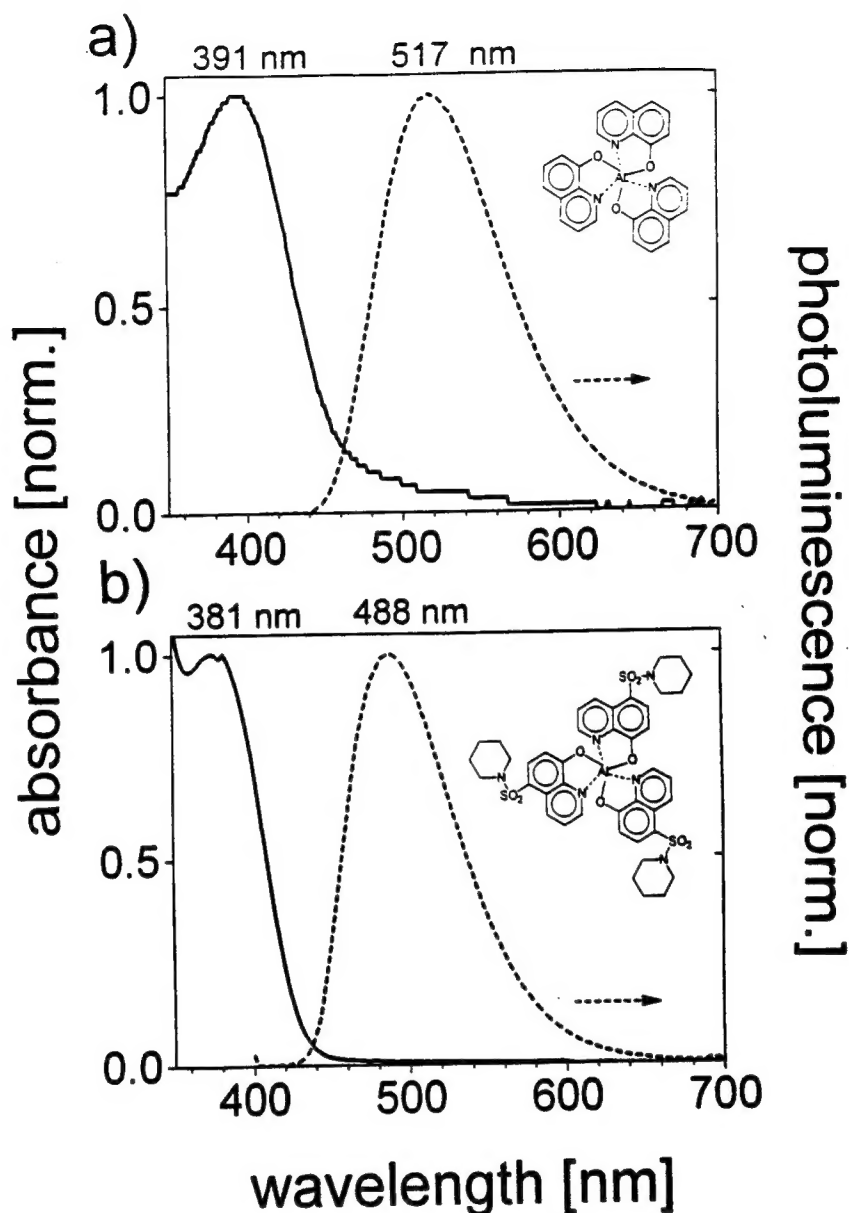


Fig. 1: Absorption and photoluminescence spectra of (a) Alq_3 and (b) $\text{Al}(\text{qS})_3$ on sapphire.

We are exploring another synthetic route to produce a variety of 8-hydroxyquinoline derivatives with various substituents in the 5-position (Scheme II). The key intermediate is the 5-lithioquinoline. The latter is obtained by reacting 8-hydroxy-5-iodoquinoline (which was synthesized from 8-hydroxyquinoline through iodination with N-iodosuccinimide in about 90% yield) with butyllithium. The lithioquinoline can then be quenched with a variety of

electrophiles such as alkyl bromides and alkyl disulfides, acichlorides, and chloroformates, thus opening up a large number of synthetic possibilities. Thus far, we have tested the viability of this route by proton quenching to obtain the educt 8-hydroxyquinoline. Work on this route is in progress.

B) Development of the state-of-the-art technology required to produce prototype devices under controlled atmosphere.

Figure 2 shows a schematic of the glove box/sample preparation facility which was constructed with partial support from ONR and partial support from the Optical Sciences Center and the University of Arizona. It is clear that the ability to make LED devices under controlled atmosphere conditions will be critical to the success of this project. At the present time, this chamber is essentially complete and is in its final testing stages.

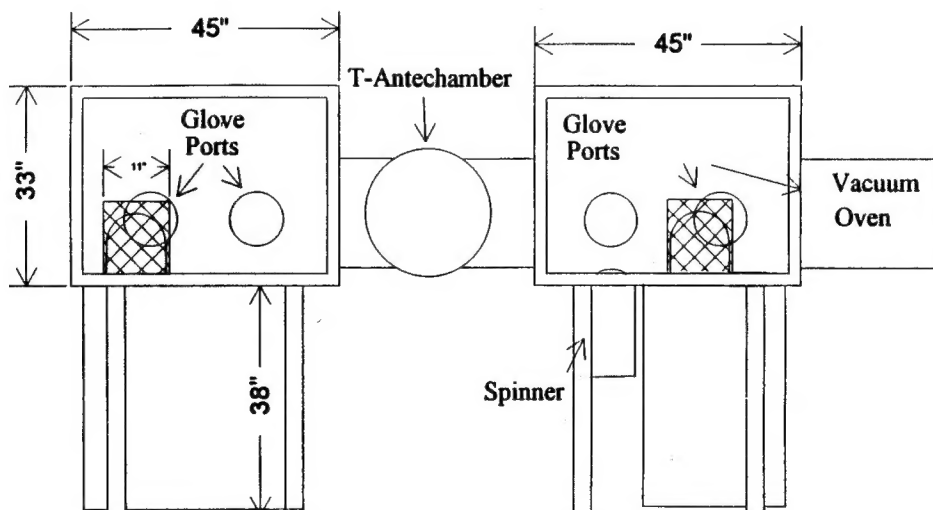


Fig. 2: Front view of the glove box system for the fabrication of organic LED/laser devices under controlled atmosphere.

The glove box system consists of two compartments. One part including a spin-coater, a vacuum oven and a vacuum evaporator is currently used to prepare various kinds of organic multilayers on a conducting substrate: the second contains another evaporator for the deposition of metal contacts and will also be used to perform characterization experiments with the fabricated devices. A window in the back of the second box allows to couple light in and out of the box. The first samples prepared in this environment showed reasonable chemical stability during operation (several minutes to hours) for this early stage of operation.

C) Characterization of the "band edges" for various electroluminescent materials and charge transport agents

The electroluminescent and diode current/voltage behavior of any organic LED is critically dependent upon the "band edge" positions of the luminescent layer and the transport layers, and the work functions of the contacting electrodes. There is only a limited understanding of these band edge positions for the organic electroluminescent systems that have been explored to date, and a definite lack of quantitative information regarding the candidate materials. Design of new luminescent and charge transport materials is critically dependent upon our ability to correlate diode performance with the mismatch between frontier orbital positions of the organic layers in existing diodes.

We have undertaken to create a band edge picture for an existing diode technology, a 3-layer device consisting of a luminescent layer cladded between an electron and an hole conducting layer. Using our UV-photoelectron spectroscopic facilities, we are able to measure HOMO positions for a variety of organic thin film materials, and to measure the onset potentials for ionization of these compounds. In addition, we have coupled these measurements with characterization of the absorbance/luminescence spectra of these systems, so as to provide an estimate of the LUMO positions, and thereby be able to approximate the energy levels for free electrons and holes, following injection from contacting electrodes.

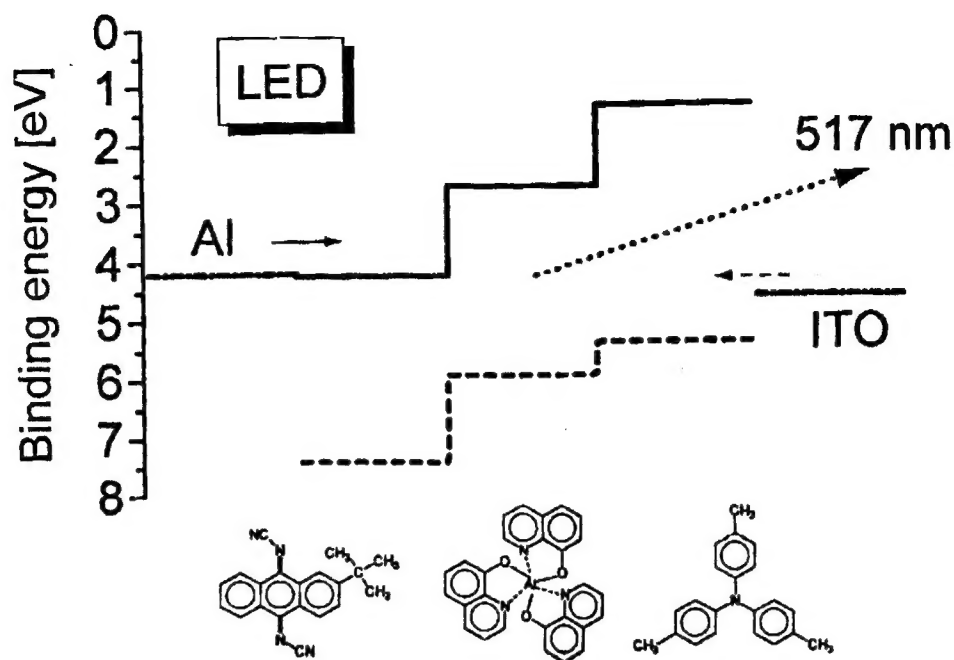


Fig. 2: Energy level diagram of a three layer LED

To demonstrate the power of the proposed method in predicting the performance of a possible LED structure we have assumed a three-layer system shown in Figure 2. The device is based upon Alq_3 , and typical hole and electron transport materials (tris(4-methylphenyl)amine, TTA, and 2-tert-butyl-9,10-N,N'-dicyanoanthraquinonediimine, DCAQ, respectively) that are currently used in the photocopier industry. Aluminum was assumed to be the rectifying contact for electron injection, and optically transparent ITO to be the ohmic contact for hole injection. The relatively low barrier toward electron injection from the Al electrode to the electron transport layer is clear, as is the much higher barrier (ca. 1.5 volts) that these electrons need to overcome in order to transport into the Alq_3 layer. There are two small barriers for the holes, one is the injection from the ITO layer (ca. 0.5 volts), the other one at the interface between the hole transport layer and the Alq_3 layer (ca. 0.3 volts). Thus, recombination events are expected to occur at the interface between the Alq_3 layer and the electron transport layer due to the fact that this is the largest barrier in the whole device.

Models such as this predict much smaller turn on voltages for LED's than have been observed, but of course do not take into account the resistivity in each transport layer, the contact resistances in each device, and the role that charge trap states are likely to play in mediating charge transport in the organic matrix (e.g. the role played by O₂ in any device which has seen even a few millitorr of atmosphere exposure). Investigations are underway to now develop this model for a variety of electroluminescent systems and transport agents, and to correlate the band edge positions shown here with device performance.

D) Fabrication and characterization of blue-green emitting LED's: preliminary results

The objectives for this phase of the project are to quickly determine the suitability of different charge transport agents and luminescent materials for incorporation into our new organic LED/lasers. This involves fabrication of organic LED/laser by vacuum deposition methods and by spin-coating techniques. We have focused most of our attention on the aluminum quinolate materials, since their luminescence efficiencies are high, and because we believe that modifications of this molecule, incorporated in polymer matrices, will be the first effective organic LED/laser. We are also in the process of evaluating some new electrolumophors, which lend themselves to the vacuum deposition method. Below is a summary of the procedure for the fabrication of these devices and a description of the variety of devices made.

Organic thin film diode devices were fabricated from a variety of hole and electron transport agents and luminescence materials listed in Table 1. Suitably cleaned indium tin oxide coated glass (ITO) was used as the optically transparent conductive substrate which served as a window to view the electroluminescence. Depositions were carried out in a specially designed vacuum chamber which consists of a series of six way stainless steel crosses pumped by a turbo molecular pump. This design allows multilayer deposition from up to 3 organic sources and 1 metal source, and is a direct extrapolation from technology developed here to do organic thin film formation by Organic Molecular Beam Epitaxy (OMBE).

Characterization of LED's was carried out in glove bags, while our glove box technology comes on line as described in section B.

Table 1. Description of the devices fabricated and tested to date; HTA and ETA are hole and electron transport agents, respectively.

Device	HTA	Lumophor	ETA	Cap Electrode	Emission Color
I	TPD	Alq ₃	none	Al	green
II	TPD	Alq ₃	none	Mg	green
III	none	Alq ₃	none	Al	green
IV	none	Al(qS) ₃ / PVK	none	Al	blue-green
V	TPD	DNA	PBD	Al	blue-green

The type I devices made with Alq₃ , N,N'-diphenyl-N,N',-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, Kodak OP32), and Al rectifying contacts showed electroluminescence in the green at onset voltages of 14 V. At a drive voltage of 16 V, the device I emits for 18 hours when tested in a glove bag filled with nitrogen. In contrast, in air the electroluminescence efficiency decays rapidly within a few seconds and a dark areas in the active region can be observed. Devices with magnesium electrodes (type II) have also been fabricated to lower the onset voltages, but the stability of these devices is even shorter than the one of their analogs with an aluminum top electrode. The oxidation of the magnesium is probably at the origin of the poor performance of these devices. We are now evaluating alloys

of magnesium and silver to provide simultaneously low work function and good chemical stability.

Devices **I** to **III** are all fabricated by vacuum evaporation techniques. A parallel approach is being currently followed in which the modified lumophor (an electron conductor) described in section A is dissolved in a hole conducting matrix, namely PVK (poly(N-vinylcarbazole)). Such devices (type **IV**) are fabricated by spin-coating the luminescent material and by evaporating a top Al electrode. These devices exhibit an photoluminescence spectrum that is blue shifted by 29 nm with respect to the emission of type **III** devices as shown Figure 1. The emission in the blue-green looks very promising and its characterization is under progress.

One of the new compounds currently being evaluated as an electrolumophor is 2,2'-dihydroxy-1,1'-naphthalazine (DNA). This compound has a fluorescence quantum efficiency in the solid state of near 100%, and can be vacuum deposited readily to provide electroluminescent thin films. It is currently in widespread use as a UV sensitizer for CCD cameras, and is readily available at low cost. 3-Layer devices (type **V**) using TPD and the oxadiazole derivative PBD have been fabricated and they show promising blue-green electroluminescence similar to those made from $\text{Al}(\text{qS})_3$ devices (type **IV**). We are exploring ways to optimize its efficiency, and to incorporate it, or a derivative, into a polymeric matrix.

Despite their encouraging brightness, all these devices have a relatively short lifetime to be characterized in detail but the ability to produce them soon in the glove box preparation unit looks very promising. Encapsulation of these devices, once formed in the glove box, to provide sufficient lifetime for external characterization, is also under progress.

Additional areas of focus include measuring hole and electron mobilities in the organic thin films, optical gain measurements, and absorption losses of waveguides formed with the best lumophor candidates.